

**Supplementary Table A: Criteria for ABC Classification<sup>1</sup>**

| Impact category                               | Class A                                                                         | Class B                                                                         | Class C                                                           |
|-----------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Land use                                      | $\geq 100 \text{ m}^2 \text{ kg}^{-1}$                                          | $\geq 10 \text{ m}^2 \text{ kg}^{-1}$ and $< 100 \text{ m}^2 \text{ kg}^{-1}$   | $< 10 \text{ m}^2 \text{ kg}^{-1}$                                |
| Raw material availability                     | Non-renewable resources, predicted exhaustion within 30 years                   | Non-renewable resources, predicted exhaustion in 30-100 years                   | Renewable resources, guaranteed long term supply ( $> 100$ years) |
| Complexity of the synthesis                   | $> 10$ stages                                                                   | 3-10 stages                                                                     | $< 3$ stages                                                      |
| Thermal risk <sup>2,3</sup>                   | R1-9, 11, 12, 14-19, 30, 44<br>F <sup>+</sup> , E                               | R 10<br>F, O                                                                    | No or negligible thermal risks                                    |
| Acute toxicity <sup>2,3,4</sup>               | T <sup>+</sup> , T<br>R23-29, 31, 32, 35, 39, 42, 43, 50<br>CH-poison class 1,2 | Xn, Xi, C<br>R20-22, 34-38, 41, 63, 65-67<br>CH-poison class 3,4                | CH-poison class 5                                                 |
| Chronic toxicity <sup>2,3,5</sup>             | MAK $< 1 \text{ mg/m}^3$<br>R33, 40, 45-49, 60, 61, 64<br>T, T <sup>+</sup>     | MAK 1-10 $\text{mg/m}^3$<br>R 53, 58, 62, 63<br>X <sub>n</sub> , X <sub>i</sub> | MAK $> 10 \text{ mg/m}^3$                                         |
| Biological risk <sup>6</sup>                  | Biosafety level 3, 4                                                            | Biosafety level 2                                                               | Biosafety level 1                                                 |
| Ecotoxicity <sup>2,7</sup>                    | R 50, WGK 3                                                                     | R 51, 52, 54-57<br>WGK 2                                                        | WGK 1                                                             |
| Global warming potential (GWP)                | GWP $> 20$                                                                      | GWP $< 20$                                                                      | No global warming potential                                       |
| Ozone depletion potential (ODP)               | ODP $> 0.5$                                                                     | ODP $< 0.5$                                                                     | No ozone depletion potential                                      |
| Photochemical ozone creation potential (POCP) | POCP $> 30$ or $\text{NO}_x$                                                    | $30 > \text{POCP} > 2$                                                          | POCP $< 2$ or no effect known                                     |
| Odor                                          | Odor threshold $< 10 \text{ mg/m}^3$                                            | Odor threshold $< 500 \text{ mg/m}^3$                                           | Odor threshold $> 500 \text{ mg/m}^3$ or odorless                 |
| Eutrophication potential                      | N-content $> 0.2$ or P-content $> 0.05$                                         | N-content $< 0.2$ or P-content $< 0.05$ or C-content $> 0.2$                    | Nitrogen and phosphate-free compounds                             |

<sup>1</sup> Criteria are based on E. Heinzle, A. Biwer, M. Eissen and M. A. Kholiq, *Chem. Ing. Tech.*, 2006, **78**, 301-305.

<sup>2</sup> Standard Risk phrases (R phrases) as defined by and commonly used in the countries of European Union. For definition of R-phrases consult the EU directive on dangerous substances (67/548/EEC, Annex III; [http://ec.europa.eu/environment/chemicals/dansub/consolidated\\_en.htm](http://ec.europa.eu/environment/chemicals/dansub/consolidated_en.htm))

<sup>3</sup> Official abbreviations for the classification of chemicals according to EU directive on dangerous substances (67/548/EEC, Annex I; [http://ec.europa.eu/environment/chemicals/dansub/consolidated\\_en.htm](http://ec.europa.eu/environment/chemicals/dansub/consolidated_en.htm)). F<sup>+</sup> = extremely flammable; E = explosive; F = flammable; O = oxidizing; T<sup>+</sup> = very toxic; T = toxic; X<sub>n</sub> = harmful; X<sub>i</sub> = irritant; C = corrosive.

<sup>4</sup> Swiss poison class (CH-poison class) rating appears on European Material Safety Data Sheets (MSDS). The rating reflects the acute oral lethal dose (usually in rats): Class 1: 0-5  $\text{mg kg}^{-1}$ ; Class 2: 5-50  $\text{mg kg}^{-1}$ ; Class 3: 50-500  $\text{mg kg}^{-1}$ ; Class 4: 500-2000  $\text{mg kg}^{-1}$ ; Class 5:  $> 2000 \text{ mg kg}^{-1}$ .

<sup>5</sup> MAK (maximale Arbeitsplatzkonzentration) = German workplace threshold value

<sup>6</sup> Biosafety level defined by Centers for Disease Control and Prevention (United States) was adapted in the European Union. Biosafety level 1: not causing any disease; Biosafety level 2: moderate potential hazard to personnel and environment; Biosafety level 3: serious or potentially lethal disease as a result of exposure by inhalation; Biosafety level 4: aerosol-transmitted severe to fatal disease (no vaccines or treatment available).

<sup>7</sup> WGK (Wassergefährdungsklasse) = German water hazard classification. WGK 1: low hazard to waters; WGK 2: hazard to waters; WGK: severe hazard to waters.

[illegible]

**Supplementary Table C: Detailed mass-balances for all (S)-styrene oxide production processes**

|                                        | Ferric phenanthroline process      |                                    | Titanium silicate process          |                                    | Manganese sulfate process          |                                    | Biotechnological process           |                                    |
|----------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
|                                        | input                              | output                             | input                              | output                             | input                              | output                             | input                              | output                             |
|                                        | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> | /kg kg <sub>so</sub> <sup>-1</sup> |
| (R)-1-phenyl-1,2-ethanediol            | 0.00                               | 1.08                               | 0.00                               | 1.13                               | 0.00                               | 1.12                               | -                                  | -                                  |
| (R)-styrene oxide                      | 0.00                               | 0.06                               | 0.00                               | 0.02                               | 0.00                               | 0.03                               | -                                  | -                                  |
| (S)-1-phenyl-1,2-ethanediol            | 0.00                               | 0.00                               | 0.00                               | 0.00                               | 0.00                               | 0.00                               | -                                  | -                                  |
| (S)-styrene oxide                      | 0.00                               | 1.00                               | 0.00                               | 1.00                               | 0.00                               | 1.00                               | 0.00                               | 1.00                               |
| (salen)Co <sup>II</sup> catalyst       | 0.01                               | 0.01                               | 0.01                               | 0.01                               | 0.01                               | 0.01                               | -                                  | -                                  |
| 2-phenylethanol                        | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.00                               | 0.12                               |
| 50% hydrogen peroxide                  | -                                  | -                                  | 0.31                               | 0.05                               | 1.33                               | 0.76                               | -                                  | -                                  |
| acetic acid                            | 0.01                               | 1.60                               | 0.01                               | 0.01                               | 0.01                               | 0.01                               | 0.00                               | 0.05                               |
| acetonitrile                           | 0.49                               | 0.49                               | 0.12                               | 0.12                               | -                                  | -                                  | -                                  | -                                  |
| ammonia                                | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.08                               | 0.01                               |
| benzaldehyde                           | -                                  | -                                  | 0.00                               | 0.06                               | -                                  | -                                  | -                                  | -                                  |
| bis(2-ethylhexyl)phthalate             | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.88                               | 0.88                               |
| carbon dioxide                         | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.00                               | 1.43                               |
| citric acid                            | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.02                               | 0.02                               |
| diammonium hydrogen phosphate          | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.06                               | 0.06                               |
| <i>Escherichia coli</i> JM101 (pSPZ10) | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.00                               | 0.54                               |
| ferric phenanthroline catalyst         | 0.09                               | 0.09                               | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  |
| formaldehyde                           | -                                  | -                                  | 0.00                               | 0.02                               | -                                  | -                                  | -                                  | -                                  |
| glucose                                | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 1.69                               | 0.00                               |
| magnesium sulfate                      | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.04                               | 0.04                               |
| manganese sulfate                      | -                                  | -                                  | -                                  | -                                  | 0.00                               | 0.00                               | -                                  | -                                  |
| methanol                               | -                                  | -                                  | 0.12                               | 0.12                               | -                                  | -                                  | -                                  | -                                  |
| octane                                 | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.05                               | 0.05                               |
| oxygen                                 | 0.00                               | 0.00                               | 0.02                               | 0.00                               | 0.00                               | 0.00                               | 1.13                               | 0.00                               |
| peracetic acid                         | 4.03                               | 2.01                               | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  |
| phenyl acetaldehyde                    | 0.00                               | 1.18                               | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  |
| potassium hydrogen phosphate           | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.19                               | 0.19                               |
| sodium bicarbonate                     | -                                  | -                                  | -                                  | -                                  | 0.80                               | 0.80                               | -                                  | -                                  |
| styrene                                | 2.76                               | 0.00                               | 1.89                               | 0.09                               | 1.85                               | 0.11                               | 1.00                               | 0.03                               |
| thiamine hydrochloride                 | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.00                               | 0.00                               |
| titanium silicate catalyst             | -                                  | -                                  | 0.03                               | 0.03                               | -                                  | -                                  | -                                  | -                                  |
| toluene                                | 0.05                               | 0.05                               | 0.05                               | 0.05                               | 0.05                               | 0.05                               | -                                  | -                                  |
| urea                                   | -                                  | -                                  | -                                  | -                                  | 2.83                               | 2.83                               | -                                  | -                                  |
| US* trace elements                     | -                                  | -                                  | -                                  | -                                  | -                                  | -                                  | 0.00                               | 0.00                               |
| water                                  | 8.72                               | 8.58                               | 0.48                               | 0.33                               | 5.92                               | 6.07                               | 15.92                              | 16.65                              |
| sodium hydroxide (CIP)                 | 0.00                               | 0.00                               | 0.00                               | 0.00                               | 0.00                               | 0.00                               | 0.04                               | 0.04                               |
| water (CIP)                            | 0.23                               | 0.23                               | 0.18                               | 0.18                               | 0.19                               | 0.19                               | 4.91                               | 4.91                               |
| <b>sum</b>                             | <b>16.15</b>                       | <b>16.15</b>                       | <b>3.04</b>                        | <b>3.04</b>                        | <b>12.80</b>                       | <b>12.80</b>                       | <b>21.07</b>                       | <b>21.07</b>                       |
| <b>sum (including CIP)</b>             | <b>16.39</b>                       | <b>16.39</b>                       | <b>3.22</b>                        | <b>3.22</b>                        | <b>12.98</b>                       | <b>12.98</b>                       | <b>26.02</b>                       | <b>26.02</b>                       |

**Supplementary Table D: Environmental indices for all (S)-styrene oxide production processes**

|                                         | Ferric phenanthroline process |              |              | Titanium silicate process |             |             | Manganese sulfate process |              |              | Biotechnological process |              |             |
|-----------------------------------------|-------------------------------|--------------|--------------|---------------------------|-------------|-------------|---------------------------|--------------|--------------|--------------------------|--------------|-------------|
|                                         | input                         | output       | total        | input                     | output      | total       | input                     | output       | total        | input                    | output       | total       |
| (R)-1-phenyl-1,2-ethanediol             | 0.00                          | 4.58         | 2.75         | 0.00                      | 4.79        | 2.88        | 0.00                      | 4.74         | 2.85         | -                        | -            | -           |
| (R)-styrene oxide                       | 0.00                          | 2.98         | 1.79         | 0.00                      | 0.94        | 0.57        | 0.00                      | 1.42         | 0.85         | -                        | -            | -           |
| (S)-1-phenyl-1,2-ethanediol             | 0.00                          | 0.01         | 0.01         | 0.00                      | 0.01        | 0.00        | 0.00                      | 0.01         | 0.00         | -                        | -            | -           |
| (S)-styrene oxide                       | 0.00                          | 46.24        | 27.75        | 0.00                      | 46.24       | 27.75       | 0.00                      | 46.24        | 27.75        | 0.00                     | 46.24        | 27.75       |
| (salen)Co <sup>II</sup> catalyst        | 0.27                          | 0.26         | 0.26         | 0.28                      | 0.27        | 0.28        | 0.28                      | 0.27         | 0.27         | -                        | -            | -           |
| 2-phenylethanol                         | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.00                     | 0.49         | 0.30        |
| 50% hydrogen peroxide                   | -                             | -            | -            | 10.88                     | 1.19        | 5.07        | 45.96                     | 19.18        | 29.89        | -                        | -            | -           |
| acetic acid                             | 0.15                          | 29.21        | 17.59        | 0.15                      | 0.15        | 0.15        | 0.15                      | 0.14         | 0.15         | 0.00                     | 0.90         | 0.54        |
| acetonitrile                            | 2.47                          | 6.38         | 4.82         | 0.62                      | 1.60        | 1.21        | -                         | -            | -            | -                        | -            | -           |
| ammonia                                 | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 2.96                     | 0.43         | 1.44        |
| benzaldehyde                            | -                             | -            | -            | 0.00                      | 0.30        | 0.18        | -                         | -            | -            | -                        | -            | -           |
| bis(2-ethylhexyl)phthalate              | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 31.15                    | 22.94        | 26.22       |
| carbon dioxide                          | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.00                     | 4.06         | 2.44        |
| citric acid                             | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.06                     | 0.07         | 0.07        |
| diammonium hydrogen phosphate           | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.10                     | 0.57         | 0.38        |
| <i>Escherichia coli</i> JM101 (pSPZ10)  | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.00                     | 5.28         | 3.17        |
| ferric phenanthroline catalyst          | 1.80                          | 2.10         | 1.98         | -                         | -           | -           | -                         | -            | -            | -                        | -            | -           |
| formaldehyde                            | -                             | -            | -            | 0.00                      | 0.56        | 0.34        | -                         | -            | -            | -                        | -            | -           |
| glucose                                 | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 1.69                     | 0.00         | 0.67        |
| magnesium sulfate                       | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.07                     | 0.04         | 0.05        |
| manganese sulfate                       | -                             | -            | -            | -                         | -           | -           | 0.05                      | 0.04         | 0.04         | -                        | -            | -           |
| methanol                                | -                             | -            | -            | 2.44                      | 1.89        | 2.11        | -                         | -            | -            | -                        | -            | -           |
| octane                                  | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 1.85                     | 1.84         | 1.85        |
| oxygen                                  | 0.00                          | 0.00         | 0.00         | 0.05                      | 0.00        | 0.02        | 0.00                      | 0.00         | 0.00         | 2.80                     | 0.00         | 1.12        |
| peracetic acid                          | 136.65                        | 58.07        | 89.50        | -                         | -           | -           | -                         | -            | -            | -                        | -            | -           |
| phenyl acetaldehyde                     | 0.00                          | 4.59         | 2.76         | -                         | -           | -           | -                         | -            | -            | -                        | -            | -           |
| potassium hydrogen phosphate            | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.19                     | 1.84         | 1.18        |
| sodium bicarbonate                      | -                             | -            | -            | -                         | -           | -           | 0.80                      | 0.80         | 0.80         | -                        | -            | -           |
| styrene                                 | 60.27                         | 0.00         | 24.11        | 41.36                     | 1.89        | 17.68       | 40.33                     | 2.22         | 17.46        | 21.79                    | 0.62         | 9.09        |
| thiamine hydrochloride                  | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.00                     | 0.00         | 0.00        |
| titanium silicate catalyst              | -                             | -            | -            | 0.41                      | 0.38        | 0.39        | -                         | -            | -            | -                        | -            | -           |
| toluene                                 | 1.13                          | 0.87         | 0.97         | 1.05                      | 0.82        | 0.91        | 1.15                      | 0.89         | 0.99         | -                        | -            | -           |
| urea                                    | -                             | -            | -            | -                         | -           | -           | 2.83                      | 27.48        | 17.62        | -                        | -            | -           |
| US* trace elements                      | -                             | -            | -            | -                         | -           | -           | -                         | -            | -            | 0.01                     | 0.02         | 0.02        |
| water                                   | 8.72                          | 8.58         | 8.63         | 0.48                      | 0.33        | 0.39        | 5.92                      | 6.07         | 6.01         | 15.92                    | 16.65        | 16.36       |
| sodium hydroxide (CIP)                  | 0.04                          | 0.03         | 0.03         | 0.03                      | 0.02        | 0.02        | 0.03                      | 0.02         | 0.03         | 0.79                     | 0.58         | 0.66        |
| water (CIP)                             | 0.23                          | 0.23         | 0.23         | 0.18                      | 0.18        | 0.18        | 0.19                      | 0.19         | 0.19         | 4.91                     | 4.91         | 4.91        |
| <b>Environmental factor</b>             | <b>211.5</b>                  | <b>163.9</b> | <b>182.9</b> | <b>57.7</b>               | <b>61.4</b> | <b>59.9</b> | <b>97.5</b>               | <b>109.5</b> | <b>104.7</b> | <b>78.6</b>              | <b>102.0</b> | <b>92.6</b> |
| <b>Environmental factor (incl. CIP)</b> | <b>211.7</b>                  | <b>164.1</b> | <b>183.2</b> | <b>58.0</b>               | <b>61.6</b> | <b>60.1</b> | <b>97.7</b>               | <b>109.7</b> | <b>104.9</b> | <b>84.3</b>              | <b>107.5</b> | <b>98.2</b> |